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Pernanganometric Method of Winkler's
Determination of Oxygen Content

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Budapest, May 1951

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PERMANGANOMETRIC METHOD OF WINKLER'S DETERMINATION OF OXYGEN CONTENT.

(This paper was first published in Zeitschrift für analytische Chemie, Vol. 127, pp. 192-196, in September 1944. Due to the war this issue of the above journal has been virtually destroyed; moreover, the copy made of the original manuscript has been lost. A variation of the text is herein published in Hungarian. Based on a copy uncovered after prolonged research, the material is republished in view of the time-saving possibilities mentioned therein. THE AUTHOR.)

Leithe (W. Leithe: Chemie Vol. 56, pp. 151, 235, 1943.) was one of the many investigators who described a method for determining oxygen dissolved in water or in a gaseous state oxidimetrically, without the use of iodine. The essential feature of this method consists in the fact that ferrous-II-hydroxide picks up the free oxygen; the excess unoxidized ferrosalts are then backtitrated with permanganate. Leithe himself gave a detailed description of the difficulties inherent in the execution of this simple conception in his above-mentioned paper. It suffices to point out ~~there~~ that using manganous-II-hydroxide provides two great advantages over ferrous-II-hydroxide. In the first place, the absorption of oxygen takes place more rapidly and, in the second place, the initial solution of the manganous-II-salt can be preserved unchanged. In using Leithe's process we are obliged to employ a rather unstable ferrous salt solution in an exactly measured amount, as the basic solution.

In view of the fact that iodine is very expensive and involves difficulties in its practical application, we have attempted to transform Winkler's iodometric method of determining oxygen into an oxidimetric method. This can be easily done since the manganic-III-compounds can be effectively reduced by means of oxalic acid, thus making their determination readily possible.

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The carefully measured out and standardized oxalic acid solution is stable and in the test is added only at the conclusion of the determination, so that any change in oxygen content can be practically eliminated. This fact has not always been true of Leithe's method.

Siegert's process (Chr. Siegert: Angew. Chem., Vol. 53, p. 235, 1940.) is based on the same conception, with the difference, however, that this investigator first reacts the manganous-II-hydroxide to prepare an equivalent quantity of potassium bicarbonate. This process not only slows down the method, but may also be responsible for gross experimental errors. In the first place, air bubbles adhering to the minute potassium bicarbonate crystals may well carry additional amounts of oxygen to the manganous-II-hydroxide and, in the second place, an overflowing of the solution above the precipitate, may result in the loss of a small amount of manganous-II-hydroxide, due to the fact that minor remnants of the precipitate remain suspended in the solution even after having been allowed to stand half an hour. (In one of our experiments the solution above the precipitate was transferred, by means of a suction tube, into an acidified potassium iodide solution, and 1.58 milliliters of 0.02 N thiosulfate solution was used for back-titrating the precipitated iodine. This corresponds to 0.68 milliliters of oxygen. As 5.56 milliliters of oxygen were found in connection with the titration of the precipitate remaining in the flask used for oxygen determination, the sum of these two figures yields 6.24 milliliters of oxygen found iodometrically.) It will be seen from our experiments described below that the previous change of manganous hydroxide into carbonate is superfluous, due to the fact that acidification results in a solution entirely indifferent to oxygen, the oxidizing capacity of which is exactly equivalent to the amount of oxygen originally present.

In producing manganous hydroxide we mix concentrated sodium hydroxide, free of potassium iodide, with the solution of manganous-II-salts. After the precipitate has settled, we add sulphuric acid, pouring the brown-colored

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solution, in which the still undissolved manganic-III-hydroxide particles are suspended, into the oxalic acid solution the amount of which has previously been ascertained. By heating the solution mildly to 35-40 degrees Centigrade, it is made entirely clear, enabling us to back-titrate the excess oxalic acid by means of permanganate. In order to obtain as correct results as possible, 0.02 N solutions should be used. The final phase of titration can be ascertained accurately to 1-2 drops by using solutions of such concentrations in liquid volumes of 3 - 500 milliliters.

According to the data published by Treadwell, oxalic acid is much more stable in the presence of sulphuric acid than in pure solutions. After measuring out the required amount of oxalic acid, it is dissolved in distilled water and then poured into an equal volume of sulphuric acid of such strength as to assure that every liter of solution will contain 50 milliliters of concentrated acid. No change whatsoever can be observed over long periods in the standard of a solution prepared in accordance with these instructions.

The titer of the 0.02 N permanganate is first adjusted iodometrically; it can always be adjusted again and controlled subsequently with respect to oxalic acid. No significant changes have been observed in the titer within the period of one week.

The presence of chloride ion in the titration process carried out by means of permanganate has a confusing effect only in the absence of manganous-II-ions. Our own experiences have shown that the manganous-II-concentration actually present is wholly sufficient for preserving the faint pink color in the lukewarm solution for one minute after concluding the titration.

The necessary data are as follows:

Sodium hydroxide solution: 325 grams of pure sodium hydroxide (not purified by means of alcohol) are dissolved in one liter of distilled water.

Manganous-II-sulfate solution: 400 grams of crystalline pure manganous-II-sulfate are dissolved in one liter of distilled water.

Concentrated sulphuric acid: It is recommended that pure sulphuric acid obtainable in the trade be used.

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0.02 N oxalic acid: 1.26 gram of pure oxalic acid is dissolved in 400-500 milliliters of distilled water, to which we add 50 milliliters of concentrated sulphuric acid and then dilute the whole to one liter of solution.

0.02 normal permanganate solution: The 0.1 N solution is diluted five-fold.

Determination of oxygen dissolved in water is carried out in the following manner:

1. Adjusting the titer of the oxalic acid solution.

In order to ascertain the proportion of the oxalic acid solution with respect to the 0.02 N permanganate solution, we measure out 20 milliliters of sulphuric-0.02 N oxalic acid into a wide-necked Erlenmeyer flask, to which we add first 250 - 300 milliliters of tap water and then 5 milliliters of concentrated sulphuric acid, 3 milliliters of sodium hydroxide solution, and after shaking we add 3 milliliters of the manganous-II-salt solution (the sequence must be strictly observed!). The flask is heated to 35 - 40 degrees Centigrade over a wire gauze and the contents are then titrated with 0.02 N permanganate. The process of titration can be considered concluded when the solution remains tinted for one-half minute.

2. Determination of dissolved oxygen.

We transfer by pipette 3 milliliters of sodium hydroxide solution into the specimen selected according to the general instructions. We add immediately by a pipette 3 milliliters of manganous-II-salt solution to the bottom of the flask, which we close with a ground-glass stopper. Whirling the flask promotes a perfect absorption of oxygen by the precipitate. After the precipitate settles (15 to 30 minutes) we introduce 5 milliliters of concentrated sulphuric acid by the pipette over the precipitate and close and whirl the flask again so as to accelerate dissolving of the precipitate. In the meantime we measure out 20 milliliters of oxalic acid solution into a wide-necked Erlenmeyer retort, into which we then pour the acidified content of the flask used for the determination. We heat the flask to 35 - 40 degrees Centigrade

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over a wire gauze, with the result that the solution becomes entirely clear. Then we back-titrate the excess oxalic acid by means of permanganate. The difference found between the milliliters of permanganate solution (used in rendering the titer constant) and the amount of permanganate consumed in connection with back-titration reveals the equivalent of oxygen we set out to ascertain. One milliliter of 0.02 normal permanganate solution is equivalent to 0.1120 milliliters of oxygen with standard conditions prevailing.

In testing this procedure we filled a 50 liter round-bottom flask with tap water and produced different oxygen concentrations by blowing air in. We used siphons to take specimens. The control analyses yielded the following results in milliliters:

TABLE 1.

0.02 N KMnO ₄ consumed	Volume of the Flask	O ₂ per liter found permanganato- metrically	Mean Value	O ₂ per liter found iodometrically
13.95	272.20	5.86		
14.20	274.54	5.92	5.91	5.92
14.38	277.01	5.94		
15.10	277.15	6.26		
15.02	277.44	6.28	6.25	6.28
14.72	277.20	6.22		

No change was observed in the oxidizing capacity of the solution when the reduction by oxalic acid was delayed as long as 12 hours after acidification.

The iodometric method cannot be carried out when nitrite-containing water or water contaminated by organic substances is used. Our method of determination can be applied without any change whatsoever. Only one correction must be employed subsequently for improving the results obtained by measuring. This correction is readily obtained through the following procedure, the original form of which was also derived by Winkler. It should be understood that the correction must be applied in connection with our oxidimetric method.

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One milliliter of manganous-II-sulfate solution and the same amount of sodium hydroxide solution free from potassium iodide are added to 250 milliliters of distilled water. Add 250 milliliters of 10 percent sulphuric acid to the precipitate, in which 5 grams of crystalline manganous-II-sulfate have been dissolved. On clearing, we take 100 milliliters of this solution and mix it with 100 milliliters of the water to be tested, while another amount of 100 milliliters is added to 100 milliliters of distilled water. Five milliliters of oxalic acid solution are added to both specimens after five minutes. The excess amount is back-titrated with permanganate. The correction resulting from the difference between the two types of titration has the advantage of being based on the same reaction as the method for determination.

We found 5.78 milliliters of oxygen per liter in a specimen of water saturated with air at room temperature. Subsequently we dissolved 20 milligrams of sodium nitrite per liter in the same and then we determined again the oxygen content as well as the correction value by employing the method previously described. The results are contained in the following table in milliliters:

TABLE 2.

<u>0.02 N KMnO₄ Consumed</u>	<u>Correction 0.02 N KMnO₄</u>	<u>Volume of the Flask</u>	<u>O₂ found</u>
8.82	5.10	272.20	5.86
8.82		274.44	5.71

S U M M A R Y

The iodometric method of determining the amount of oxygen absorbed by water according to Winkler's method can also be carried out permanganometrically on the basis that the manganic-III-salt is equivalent to oxygen. Oxalic acid is measured out in excess and the non-oxidized portion is then back-titrated by means of potassium permanganate. In order to assure exact determinations, 0.02 Normal solutions should be used.

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